Degassing

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ABSTRACT

Measurements of the concentrations of rare gases and trace elements in oceanic basalts have provided new information concerning the structure of the Earth's mantle and its evolution. This review is based principally on papers by Allegre, Staudacher, Sarda, O'Nions, Oxburgh, and Jacobsen. Approximately 35% of the mantle lost more than 99% of its rare gas content in the first 100 million years of solar system history. A comparable volume of the mantle has also been depleted in radioactive and other large ion lithophile elements, the depleted elements being concentrated in continental crust. But depletion was a much slower process than degassing. The average age of continental crust is 1.8 billion years, but the average age of the rare gas atmosphere is 4.4 billion years. There has been very little mixing of material between the degassed and depleted portion (presumably the upper mantle) and the undegassed and relatively undepleted portion (presumably the lower mantle).

Gas fluxes from the mantle indicate that degassing today is inefficient, affecting only the top few hundred meters of oceanic crust. It is not likely that sea floor spreading processes like those now operating could have degassed the entire upper mantle within a 100 million years, even given large initial heat fluxes. At the same time, it is not likely that sea floor spreading processes could have dissipated the initial heat of a nearly molten Earth. Lava flooding could have removed initial heat efficiently and at the same time degassed the upper mantle rapidly.

Rare gases do not make an atmosphere, of course. There is new information concerning the release of carbon dioxide from the mantle. As

pointed out most forcefully by Marty and Jambon, the exogenic system (atmosphere, ocean, and sedimentary rocks) is deficient in carbon by a factor of 100 relative to rare gases when present amounts are compared with present fluxes from the mantle. It appears that carbon dioxide did not participate in the initial rapid degassing that released rare gases from the upper mantle. Instead, carbon has been modestly concentrated into the continental crust like other incompatible, but not atmophile, elements. Less than 10% of upper mantle carbon has been transferred to the crust, and the total mantle amount may be 40 times the amount in the exogenic system.

INTRODUCTION

Important new information has become available in recent years concerning the release of gases from the interior of the Earth. The most fruitful source of information has been the measurement of rare gas concentrations in sea floor basalts. The results set important constraints that need to be incorporated into any comprehensive understanding of the early history of the planets. In my review here, I will describe some of the highlights of these results and give an indication of how they are derived. I cannot provide a complete description of all of the evidence that is used to reach the conclusions presented.

RESERVOIRS

Measurements on sea floor basalts have provided clear indications of two major reservoirs within the mantle. The larger reservoir, constituting about 65% of the mantle, is undegassed and relatively undepleted in incompatible elements. The remaining 35% of the mantle was degassed very early in Earth history (within 100 million years of the beginning), and more than 99% of the initial gas content of this reservoir was released. Throughout the whole of Earth history there has been very little mixing between these reservoirs (O'Nions 1987; Anderson 1989).

These conclusions are based on measurements of the concentrations in sea floor basalts of the radioactive parent elements shown in Figure 1, along with their radiogenic daughter isotopes and non-radiogenic cousin isotopes also shown in the figure (Allegre *et al.* 1983). The important feature of these isotope systems is that the ratio of daughter/cousin increases through time as a result of the radioactive decay of the parent, and that there are no other processes that will cause the ratio of daughter/cousin to change because they are chemically and physically almost identical.

Figure 2 shows how the ratio of daughter/cousin, called ALPHA, increases at a rate that depends on the ratio of parent/cousin, called MU.

Parent	Daughter	Cousin
K40	Ar40	Ar36
U,Th	He4	He3
I129	Xe129	Xe130

- ALPHA (=DAUGHTER/COUSIN) increased by decay
- MU (=PARENT/COUSIN) determines rate of increase

FIGURE 1 Isotope taxonomy.

The solid line in the top panel of the figure shows the evolution of the amount of radiogenic ^{40}Ar resulting from the decay of radioactive ^{40}K. The bottom panel shows the evolution of the ratio of $^{40}Ar/^{36}Ar$, ALPHA. The effect of a degassing episode fairly early in Earth history is indicated by the left hand arrow labeled Degas 50%. The degassing episode reduces the concentration of ^{40}Ar by a factor of two, as shown in the top panel. Because ^{36}Ar concentration is also reduced by a factor of two there is initially no change in ALPHA. The rate of increase of ALPHA with time is larger after the degassing episode, however, because there is less ^{36}Ar in the denominator of the ALPHA ratio. This evolution is shown by the dashed line in the figure. The effect of a second degassing event at -1 billion years is also shown in the figure. The impact of the second degassing event on the evolution of ALPHA is smaller because, later in Earth history, there is less radioactive ^{40}K left to decay. Thus, early degassing leads to large increases in ALPHA; late degassing has a smaller effect. The event in the middle of Figure 2 shows the effect of a depletion by 50% in the concentration of radioactive ^{40}K. Depletion reduces the rate of increase of ALPHA in the manner indicated by the dashed line. In this way it is possible to deduce the history of MU from measurements of ALPHA.

The basic data concerning mantle degassing appear in Figure 3. They are ALPHA values measured for He, Ar, and Xe in mid-ocean ridge basalts and in ocean island basalts. The mid-ocean ridge basalts appear to sample the upper mantle, whereas the ocean island basalts are assumed

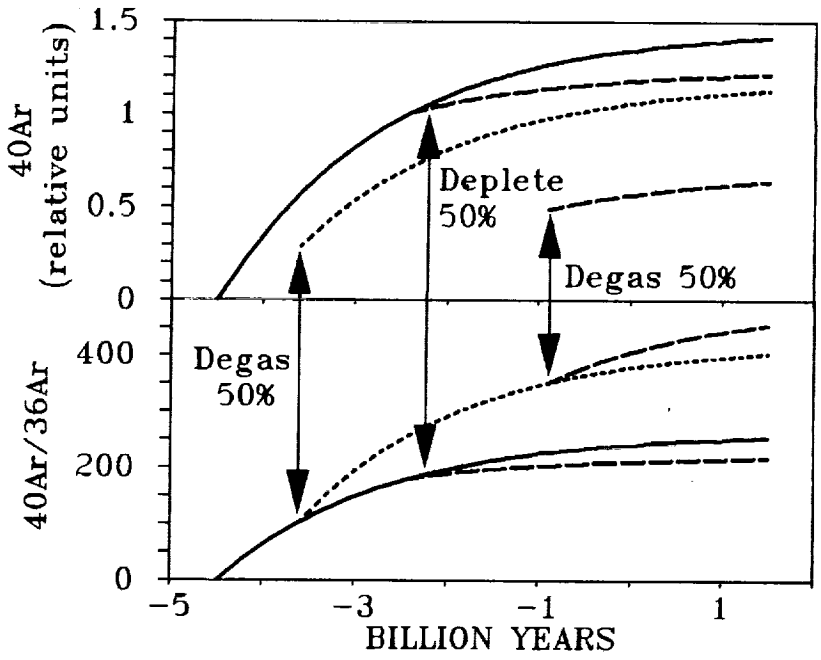

FIGURE 2 Measure ALPHA to deduce history of MU.

to sample plumes of material rising from the lower mantle. There is a range of compositions of ocean island basalts representing various degrees of mixing between lower mantle material and upper mantle material. As representative of the least contaminated material I show results for Loihi sea mount in Hawaii. The point is that ALPHA is larger in MORB than in Loihi material, which indicates that MORB material is more degassed. The enhancement in ALPHA has been large for He and Ar. From data such as these it is now possible to derive important results concerning mantle reservoirs.

First, the bulk Earth concentration of K gives the ^{40}Ar concentration in undegassed mantle material. The ALPHA value observed in Loihi basalts gives the ^{36}Ar concentration in undegassed mantle material. The mass of ^{36}Ar in the atmosphere then gives the mass of the mantle that has been degassed. From a comprehensive study of rare gas isotope systematics Allegre *et al.* (1987) deduce that 46% of the mantle has been degassed. To increase the ALPHA value of Ar from the Loihi value to the MORB value it is necessary that no more than 390/25000 = 1.6% of the initial ^{36}Ar complement be retained in degassed mantle material. This value would apply in the case of early degassing from undepleted material. Delayed degassing or prior depletion of ^{40}K would reduce the permitted degree of

ALPHA

	He	Ar	Xe
MORB	86,000	25,000	6.95
Loihi	25,000	390	6.48

- MORB samples degassed reservoir (upper mantle)
- Loihi samples undegassed (lower mantle)

FIGURE 3 Data that constrain degassing (Allegre *et al.* 1987).

retention. The conclusion is that degassing has been very thorough indeed. At the same time, because the difference between ALPHA values in Loihi and MORB is so great, it is possible to conclude that just 2% contamination of MORB material by Loihi material would reduce the ALPHA value of the degassed mantle by a factor of two. There is therefore evidence for strong isolation of the mantle reservoirs from one another.

The increase in the ALPHA value for Xe between Loihi and MORB, although modest, demonstrates that degassing took place very early in Earth history. For ALPHA to have changed, degassing must have occurred before all of the parent ^{129}I had decayed away. But the half life of ^{129}I is only 17 million years. Therefore, the division of the mantle into two reservoirs, the very thorough degassing of one of these reservoirs, and the nearly total isolation of the two reservoirs all took place very early in Earth history. At this time it is not clear to me how to reconcile these surprising conclusions with our current understanding of the growth of the Earth by planetesimal impact, in which planetesimals were vaporized and degassed, at least during the later stages of accretion. Neither is it clear how to reconcile with these data the current thinking concerning the formation of the Moon by a giant impact event occurring near the end of Earth

accretion. It appears likely that such an impact would have completely remixed and homogenized the mantle. On the other hand, it is not clear that such an impact event would have led to complete degassing of the mantle or to complete removal from the Earth of any atmosphere released during the course of previous accretion. Also unclear is what physical process causes the separation of the mantle into two distinct reservoirs. In my further analysis I shall assume that degassing of the upper mantle was a consequence of mantle convection, possibly driven by accretional energy, but that most of the impacts, and in particular the giant Moon-forming impact had already occurred before the processes that brought about the presently observable state had begun.

In this interpretation then, degassing should be related to continental growth and the depletion of the upper mantle in incompatible elements. Studies of continental growth and depletion are based on precisely the same kind of isotopic arguments as the studies of degassing already described. The only difference in depletion is that the daughter and cousin isotopes are concentrated in the continents instead of in the atmosphere. Analyses of Sm-Nd, Lu-Hf, and Rb-Sr isotopes in sea floor basalts, summarized in Figure 4, indicate that 30% of the mantle has been depleted to form the continents (Jacobsen 1988). The average age of the continents is 1.8 Ga. Allegre *et al.* (1983, 1988), in a similar analysis, conclude that 35% of the mantle has been depleted while 47% of it has been degassed (Sarda *et al.* 1985). The average age of the rare gas atmosphere deduced in their analysis is 4.4 Ga. My tentative conclusion is that the degassed and depleted reservoirs are probably the same, but that degassing occurred much earlier than depletion.

FLUXES

Fluxes of gases from the mantle to the atmosphere can be deduced from the measured flux of ^{3}He and the concentration ratios in sea floor basalts. These fluxes lead to the very interesting conclusion that heat is released much more readily from the mantle than are the rare gasses (O'Nions and Oxburgh 1983; Oxburgh and O'Nions 1987). Further it can be argued that degassing today is inefficient. Processes now operating could not have degassed the upper mantle rapidly and thoroughly. A comparison of the fluxes of heat, helium, and argon is presented in Figure 5. The sources are mainly concentrated in the lower mantle because the upper mantle is depleted in radioactive incompatible elements. The heat flux through the surface of the Earth exceeds the sum of upper and lower mantle sources because the interior of the Earth is cooling down. This fact is reflected in the Urey ratio of source/flux. For heat this ratio has a value of about 0.6 (Pollack 1980). For ^{4}He the Urey ratio is 6.8, indicating that

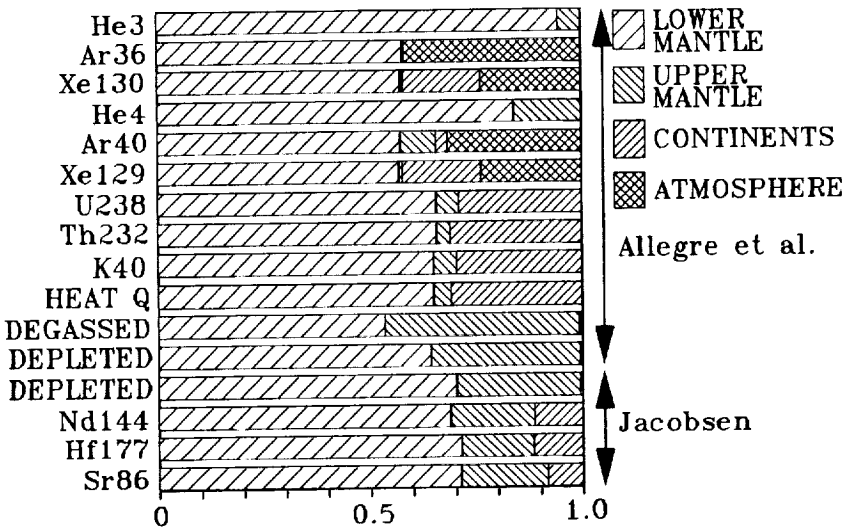

FIGURE 4 Comparison of deductions concerning degassing and depletion (Allegre *et al.* 1983, 1987; Jacobsen 1988). The bars indicate what fraction of the terrestrial complement of each isotope is in the indicated reservoir. HEAT Q refers to heat source.

most radiogenic helium is retained within the Earth and that the flux from mantle to atmosphere is much less than the production within the Earth. However, the flux does exceed upper mantle production. Helium must be flowing from the lower mantle to the upper mantle at a significant rate. For ^{40}Ar, on the other hand, the flux is less than the upper mantle source. There is no evidence of flow from lower mantle to upper mantle; the Urey ratio is 23, and ^{40}Ar is accumulating even in the depleted upper mantle. These observations provide strong support for the notion of a two-layer convective structure in the mantle.

It is entirely reasonable to suppose that heat is more mobile than helium which is in turn more mobile than argon. The argon flux from the mantle is 6.2×10^6 mole/y. The ^{40}Ar concentration in the upper mantle is 3×10^{-10} mole/g. Therefore, the rate at which upper mantle material is degassed, calculated from the ratio of these two numbers, is 2×10^{16} g/y. Since the mass of the upper mantle (35% of the total mantle) is 1.4×10^{27} g, it would take 70 Ga to degas the upper mantle at this rate. But the xenon isotope data indicate that the upper mantle was degassed in less than .1 Ga. Therefore, the present rate of degassing is too slow to explain the observations by a factor of 1000.

Furthermore, degassing today is inefficient, in the sense illustrated in Figure 6. Ocean crust is formed by the partial melting of upper-mantle

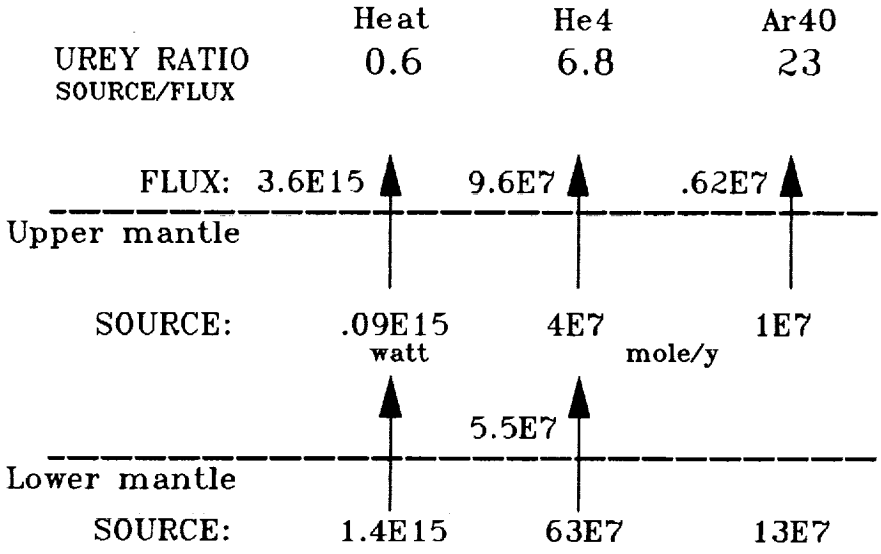

FIGURE 5 Fluxes of heat and gases and ratios of sources to fluxes.

material. The degree of partial melting can be deduced from the concentrations of the completely incompatible element potassium. Potassium concentration is enhanced in ocean crust by a factor of 10, more or less, so we have approximately a 10% partial melt of 60 kilometers of upper mantle material to produce six kilometers of ocean crust. About the same increase by a factor of 10 can be expected in the concentration of ^{40}Ar, also presumably a completely incompatible element. New ocean crust is generated at the rate of 3 km^2 per year. To produce the ^{40}Ar degassing flux of 6.2×10^6 mole per year it would be necessary to extract ^{40}Ar from just the top 250 meters of ocean crust. This extraction presumably occurs by interaction between sea water and the ocean crust. The ^{40}Ar does not diffuse directly out of the crust or bubble out of the magma. It must be extracted by leaching at relatively shallow depths in the crust. During the lifetime of the sea floor before subduction, heat will be extracted from a lithospheric layer approximately 60 kilometers thick, but Ar will be extracted only from 250 meters of ocean crust. This thickness of crust is equivalent, before partial melting, to 2.5 kilometers of upper mantle, so the release of Ar is about 25 times less efficient than the release of heat. The flux data indicate that radiogenic rare gases are accumulating in the mantle. The degassing process now operating is inefficient and slow. It seems that the process that originally degassed the upper mantle completely and rapidly must have been markedly different from the process now operating.

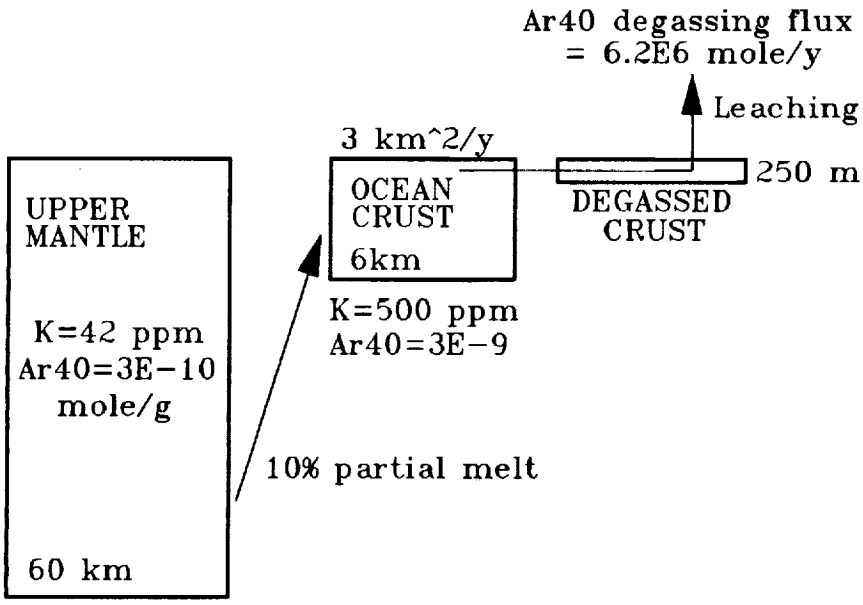

FIGURE 6 Degassing is inefficient compared with the extraction of heat.

CARBON DIOXIDE

To what extent can the rare gas results be applied to more important constituents of the atmosphere? It turns out that there is significant information concerning carbon dioxide (Des Marais 1985; Marty and Jambon 1987). The data and results are summarized in Figure 7. The flux of carbon dioxide from mantle to atmosphere today is 2×10^{12} mole per year. The flux of ^{36}Ar is 250 mole per year, so the ratio of the fluxes is 8×10^{9}. On the other hand, the ratio of the amounts in atmosphere, ocean, and continental crust is 1.8×10^{6}. The ratio of fluxes is very much larger than the ratio of amounts now present in the surface layers of the Earth. Carbon is missing from the surface layers relative to argon.

This conclusion can be seen also in the accumulation times calculated by dividing the flux into the amount. Carbon would accumulate at present rates in 5×10^{9} years, but it would take 2.2×10^{13} years for the ^{36}Ar now in the atmosphere to accumulate at the present flux. The conclusion is that while ^{36}Ar was massively degassed earlier in Earth history, carbon did not participate in this early degassing. If carbon was rapidly released from the mantle early in Earth history it was just as rapidly returned to the mantle.

Carrying this analysis further it can be concluded that carbon is a lithophile and not an atmophile element. From the flux ratio of carbon to

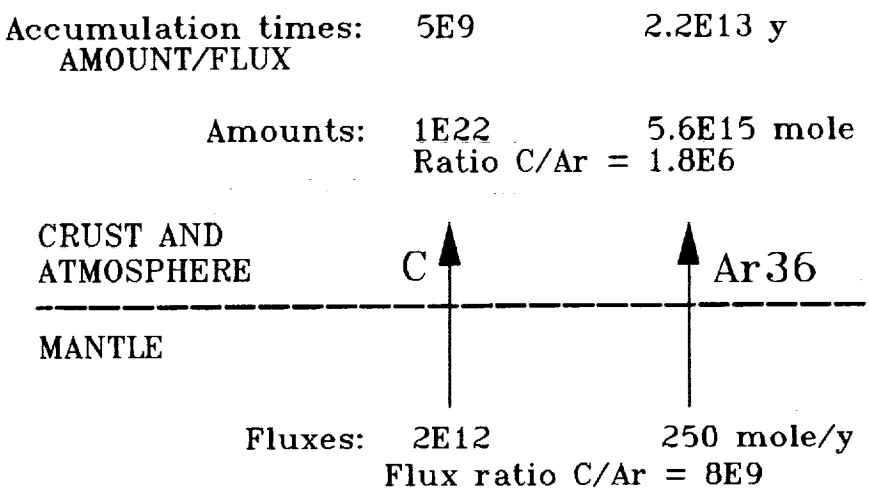

FIGURE 7 Compared to argon, carbon is deficient in the crust and atmosphere.

^{36}Ar and the concentration of ^{36}Ar in the upper mantle we can calculate the concentration of carbon in the upper mantle. The value is 1×10^{-4} mole/g. This calculation assumes that carbon is not more mobile than Ar, surely a reasonable assumption. If carbon is less incompatible than Ar the required upper mantle concentration of carbon would be larger. From the concentration and the mass of the upper mantle I calculate that there are 1.4×10^{23} moles of carbon in the upper mantle. The amount in the crust and atmosphere and ocean is only 1×10^{22} mole (Wilkinson and Walker 1989). Therefore less than 10% of upper-mantle carbon has been degassed. By way of contrast, more than 99% of upper mantle ^{36}Ar has been degassed. Continuing the analysis and assuming that the lower- mantle concentration is given by the upper-mantle concentration augmented by crustal carbon mixed back in, the total amount of carbon in the mantle is 4.2×10^{23} mole, which is 42 times the amount in crust, ocean, and atmosphere. It seems that the fate of most carbon dioxide released from the mantle is to be incorporated into oceanic crust in weathering reactions and to be carried back into the mantle on subduction. Only a small fraction of the carbon is captured in the exogenic system as cratonic carbonate rocks. The average carbon concentration in continental crust is 5×10^4 mole/g. The concentration in the upper mantle is 1×10^4 mole/g. Therefore, the crust is only moderately enriched in carbon dioxide relative to the upper mantle and, unlike the rare gases, carbon is a modestly incompatible element.

CONCLUSION

The rare gas data indicate that there was early, thorough degassing of the upper mantle, but that there remain large amounts of primordial rare gases in the undegassed, lower mantle reservoir. The time scales and rates of degassing and depletion are very different. Depletion and continental growth occurred much later in Earth history than degassing. Degassing today, by weathering of the sea floor, is a slow and inefficient process and could hardly have provided the rapid and total early degassing that apparently occurred. Carbon dioxide did not degas like the rare gasses and is only modestly incompatible in the upper mantle. With the example of carbon dioxide in mind, we must be cautious about deducing degassing histories of other important atmospheric gases like nitrogen or water from the rare gas data. In the absence of relevant observations it is not immediately clear whether other atmospheric gases have behaved more like argon or more like carbon dioxide. By analogy with the Earth, it does seem likely that large amounts of both rare gases and carbon dioxide may be retained within the interiors of Mars and Venus. This possibility must be kept in mind in the study of the origin of planetary atmospheres. I do not feel that we yet have a satisfactory description even in qualitative terms of the origin of the Earth and the atmosphere. The challenge is to reconcile the ideas of planetary growth by accretion, impact degassing during the course of accretion, the origin of the Moon by a giant impact, and the data described in this paper concerning the degassing history of the mantle.

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